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(54) Title: POLYMERIZATION CATALYSTS

(57) Abstract

The invention provides a novel olefin polymerization catalyst, in particular an olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said complexant contains a pyrazol-1-yl group substituted in the 3-position by an organic moiety containing at least 3 carbon atoms.

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Polymerization Catalysts

This invention relates to compounds useful as polymerization catalysts, and in particular to metal coordination compounds and their use as olefin polymerization catalysts.

In olefin polymerization processes, the use of catalysts is standard. In this regard both inorganic and organometallic materials have been used.

One group of catalysts of particular interest is that of the metal coordination compounds which provide homogeneous catalysts which can be used as such or can be heterogenized by loading onto a carrier material.

Typically polymerization proceeds via olefin approach to a vacant metal coordination site adjacent a metal coordinating organic group, addition of the organic group to the olefin to produce a longer organic group and to vacate a metal coordination site, approach of a further olefin to the vacated site, and so on.

The homogeneous catalysts used hitherto have included complexes of metals such as the group 4 metals Ti, Zr and Hf, generally complexed by a polydentate organic complexant which does not itself take part in the polymerization reaction but serves to block off several of the metal coordination sites. Remaining coordination sites may be occupied by organic or inorganic ligands which can be displaceable to vacate a coordination site for the catalysis reaction, or may be organic chain-initiating ligands (i.e. organic groups which may be added to the incoming olefins in the catalysis reaction), or they may be non-displaceable ligands which, like the polydentate complexants do not take part in the catalysis reaction. Generally, for a transition metal complex catalyst, the metal will have a coordination number CN given by the equation CN = (18-n)/2 where n is the number of d electrons at the metal,

with at least one monodentate ligand being an organic chain-initiating group (e.g. methyl or benzyl) or a ligand displaceable by such an organic chain-initiating ligand (e.g. a halide such as chloride).

The catalyst may be used with a co-catalyst or activator which serves to produce the organic chain-initiating group/vacant coordination site configuration. This may typically be achieved by introduction of more than one such organic group followed by removal of one to leave the requisite vacant site.

Examples of such olefin polymerization catalysts are discussed for example in US-A-4808680 (Schmidt), EP-A-482934 (Dow), US-A-5312794 (Shell) and EP-A-617052 (Asahi).

These patent publications, the disclosures whereof are incorporated herein by reference, describe various hydridotris(pyrazolyl)borate (Tp) and cyclopentadienyl (Cp) complexes of metals such as the group 4 metals titanium and zirconium. These complexes may be used on their own or together with a co-catalyst such as an alkylaluminoxane, e.g. methylaluminoxane (MAO) which is thought to methylate the complex (introducing the initial organic group for the polymerization reaction) and is thought, as a Lewis acid, to demethylate one coordination site to yield the activated catalyst and a non-coordinating anion MAO-Me^{+}. Other co-catalysts which produce cationic complexes can also be used.

We have now found that, by appropriate substitution of the non-reacting polydentate organic complexant in such metal complex catalysts, the characteristics of the polymerization process may be desirably modified. More particularly, substitution of these organic complexants with a bulky space-filling group adjacent a metal-coordinating atom enables the catalytically active site of the complex to be engineered to modify the molecular weight distribution of the olefin polymerization product. Modification of polymer molecular weight and

molecular weight distribution is desirable as it enables the properties of the polymer to be tailored in a desired manner. Thus for example increased molecular weight will lead to increased polymer melt strength which is advantageous in processing the polymer, e.g. in blow moulding. Similarly a bimodal molecular weight distribution, i.e. a distribution with lower and higher molecular weight peaks, can combine improved polymer melt strength (arising from the higher molecular weight peak) and improved flow and processability properties (arising from the lower molecular weight peak). Furthermore catalysts which are able to generate higher molecular weight polymers may be used instead to improve polymer production economics by allowing one to operate at higher reactor temperatures and thus achieve higher production rates. In this way the reduction in molecular weight that occurs in using higher reactor temperatures is offset by the increase in molecular weight achievable with such a catalyst.

While substituted Tp complexants are mentioned in the prior art, e.g. in EP-A-482931 and US-A-5312794, there is no suggestion in these documents that any benefit arises from such substitution.

Thus viewed from one aspect the invention provides an olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said complexant contains a pyrazol-1-yl group substituted in the 3-position by an organic moiety containing at least 3 carbon atoms.

Viewed from a further aspect the invention also provides a catalyst system comprising (a) a catalyst compound according to the invention and (b) a co-catalyst.

As a co-catalyst (or catalyst activator) MAO is preferred. MAO may be used as the sole co-catalyst or optionally together with another catalyst activator.

Thus besides or in addition to MAO other cation complex forming activators may also be used. In this regard mention may be made of silver and borane compounds known to the art. What is required of such alternative activators is that they should react with the organometallic catalyst to yield an organometallic cation and a non-coordinating anion (see for example the discussion on non-coordinating anions J^- in EP-A-617052 (Asahi)).

Aluminoxane co-catalysts are described by Hoechst in WO-A-94/28034. These can be linear or cyclic oligomers having up to 40, preferably 3 to 20, $\{Al(R)-O\}$ repeat units (where R is hydrogen, C_{1-8} alkyl (preferably methyl) or C_{6-18} aryl or mixtures thereof). The precise structure of aluminoxane however is unknown and, as used, a varying content of the original, unconverted aluminium compound will be present.

Viewed from a still further aspect the invention also provides a process for catalysed polymerization of olefins, characterised in that as a catalyst is used a catalyst or catalyst system according to the invention.

The catalyst of the invention thus may be a compound of formula I

$$(Cx)_n(L)_mM \qquad (I)$$

(where M is a transition metal, lanthanide or actinide; L is a mono or polydentate, preferably monodentate ligand or a mono or polyvalent non-coordinating anion; Cx is a mono or polydentate organic complexant comprising a 3-substituted pyrazol-1-yl group; n is a positive integer, preferably 1 or 2, especially 1; and m is zero or a positive integer), or a salt thereof.

The catalyst may be ionic (cationic or anionic) or non-ionic. In the case of ionic catalysts, compounds with non-coordinating counterions are preferred, and the complex formed with MAO is particularly preferred.

The values of n and m will depend upon the mono or polydentate nature and on the mono or polyvalent nature of the complexant Cx and ligands or anions L, as well as on the group to which metal M belongs. However, both n and m will generally be 4 or less.

The complexant Cx is conveniently a compound of formula II

$$X(Pz(R_1)_q)_p \qquad (II)$$

(where q is 0 or 1, at least one q being 1; p is 1, 2, 3 or 4, preferably 2, 3 or 4, especially 3; R_1 is an organic group containing at least three carbons and attached to Pz at the 3-position; and X is an organic group containing at least 3 carbons or a bridging group linking two or more pyrazol-1-yl moieties) or a salt thereof.

While mono, bis and tetra-pyrazolyl compounds of formula II may be used, it is preferred to use trispyrazolyl compounds in which at least one, and preferably all three pyrazolyl rings are 3-substituted, i.e. compounds of formula $X(Pz(R_1)_q)_3$, especially $HB(PzR_1)_3$.

The bridging group X may have a carbon skeleton, but alternatively may have as its branching site any appropriate polyvalent atom, such as boron, nitrogen, phosphorus, gallium, etc. Boron is a preferred branching site and trispyrazolylborates are especially preferred as complexants Cx.

The 3-substituent on the pyrazole ring may for example be an optionally substituted alkyl, aryl or aralkyl group. As alkyl moieties mention may be made of C_{3-20} linear, branched, cyclic or partially cyclic (e.g. cycloalkyl-alkyl) groups, in particular isopropyl, n-butyl, i-butyl, t-butyl, neopentyl, cyclohexyl and n-hexyl. Aryl moieties may be mono or polycyclic and may contain one or more heteroaryl rings, e.g. incorporating

N, O or S atoms in the aryl ring. Particular mention may be made of phenyl, 2-pyridyl, naphthyl, and anthracenyl groups.

Such alkyl and aryl groups may be substituted, e.g. to enhance their space-filling effects or to hinder rotation whereby to present a spatially restricted catalytically active site (the possible olefin coordination sites) in the catalyst. Substitution with alkyl and aryl in particular is contemplated, e.g. 2,6-dialkyl or 4-phenyl substitution of a phenyl R_1 group, e.g. to produce a bisphenyl R_1 group.

Alternatively, the R_1 group may be attached to the pyrazolyl ring at both the 3 and 4 positions to yield an annelated structure having for example a benzene, cyclohexane or naphthalene ring fused to the pyrazole ring, and optionally carrying pendant or fused ring substituents, eg. alkyl, aryl, aralkyl and alkylene groups.

Such fused substituents will conveniently comprise one or more cycloalkyl, aryl or heteroaryl rings optionally substituted, e.g. by alkyl or aryl groups.

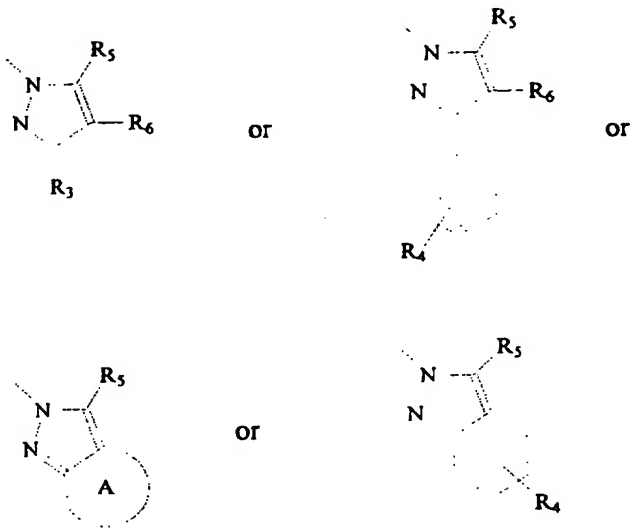
R_1 groups may thus conveniently comprise one or more, e.g. up to 4, fused or linked rings, each ring containing 5 to 9, preferably 5 to 7, ring atoms of which none, one or two may be ring heteroatoms, preferably O, N or S atoms.

Besides substitution by R_1 at the 3 (and optionally also 4) position to engineer the conformation of the catalytically active site, the pyrazole ring may be substituted at the 4 or 5 positions, e.g. to modify the solubility properties of the catalyst or to shield a bridging group X. Substitution in this regard may again be by optionally substituted alkyl, aryl or aralkyl groups, halogen atoms, carboxyl or sulphate (SO_3H) groups (or esters, amides or carboxylate salts thereof), e.g. phenyl, methyl or haloalkyl groups such as CF_3.

In general, unless otherwise stated, alkyl or

alkylene moieties in the compounds of the invention will contain up to 12, preferably up to 6, carbons, cyclic groups will have ring sizes of 5 to 9 ring atoms containing 0, 1 or 2 ring heteroatoms, and polycyclic substituent groups will contain up to 4, preferably 2 or 3, fused or non-fused rings.

Examples of preferred 3-substituted pyrazole groups PzR_1 thus include groups of formula



where R_3 is a linear or branched C_{3-8} alkyl group, R_4 is hydrogen alkyl, aryl, fused aryl or COOH or SO_3H (or salts, esters or amides thereof), R_5 is hydrogen or optionally substituted alkyl or aryl, e.g. CH_3 or CF_3, R_6 is a hydrogen or halogen atom or an alkyl, aryl or aralkyl group, and A is a C_5 or C_6 ring optionally carrying a further 4 to 6 membered fused ring and optionally substituted by R_4 or by alkyl or alkaryl groups, e.g. the groups

3-isopropyl-pyrazol-1-yl
3-tertbutyl-pyrazol-1-yl
3-neopentyl-pyrazol-1-yl
3-phenyl-pyrazol-1-yl

3-mesityl-pyrazol-1-yl
3-anisyl-pyrazol-1-yl
3-m-tolyl-pyrazol-1-yl
3-thienyl-pyrazol-1-yl
3-naphthyl-pyrazol-1-yl
3-anthracyl-pyrazol-1-yl
3-fluorenyl-pyrazol-1-yl
3,5-diphenyl-pyrazol-1-yl
5-methyl-3-phenyl-pyrazol-1-yl
5-trifluoromethyl-3-phenyl-pyrazol-1-yl
camphorpyrazol-1-yl
2R,5R-menthyl-pyrazol-1-yl
indazol-2-yl
2H-benz[G]indazol-2-yl
4,5-dihydro-2H-benz[G]indazol-2-yl
3-methyl-4,5-dihydro-2H-benz[G]indazol-2-yl and
1,4-dihydroindeno[1,2-c]pyrazol-1-yl
3-propyl-9,9-dimethyl-4,5-diazatricyclo
[6.1.0.$0^{2,6}$]non-2(6),3-dien-5-yl
(7R)-4-propyl-7-(1-methyl-1-ethenyl)-2,3-
diazabicyclo[3.3.0]oct-2-yl
7(R) or (S)-isopropyl-4(R)-methyl-4,5,6,7-tetrahydro-
indazol-2-yl
pinanyl-pyrazolyl
7(R) or (S)-tert.butyl-4(R)-methyl-4,5,6,7-tetrahydro-
indazol-2-yl and
7(R) or (S)-(1-methyl-1-phenylethyl)-4(R)-methyl-
4,5,6,7-tetrahydro-indazol-2-yl

Examples of preferred complexants Cx include

hydridotris(3-propylpyrazol-1-yl)borate
hydridotris(3-isopropylpyrazol-1-yl)borate
hydridotris(3-tert-butylpyrazol-1-yl)borate
hydridotris(3-neopentylpyrazol-1-yl)borate
hydridotris(3-phenylpyrazol-1-yl)borate
hydridotris(3-mesitylpyrazol-1-yl)borate

hydridotris(3-anisylpyrazol-1-yl)borate
hydridotris(3-m-tolylpyrazol-1-yl)borate
hydridotris(3-thienylpyrazol-1-yl)borate
hydridotris(3-naphthylpyrazol-1-yl)borate
hydridotris(3-anthracylpyrazol-1-yl)borate
hydridotris(3-fluorenylpyrazol-1-yl)borate
hydridotris(3,5-diphenylpyrazol-1-yl)borate
hydridotris(5-methyl-3-phenylpyrazol-1-yl)borate
hydridotris(3,5-di-isopropylpyrazol-1-yl)borate
hydridotris(2R,5R-menthylpyrazolyl)borate
hydridotris(indazol-2-yl)borate
hydridotris(2H-benz[G]indazol-2-yl)borate
hydridotris(4,5-dihydro-2H-benz[G]indazol-2-yl)borate
hydridotris(3-methyl-4,5-dihydro-2H-benz[G]indazol-2-yl)borate
hydridotris(1,4-dihydroindeno[1,2-c]pyrazol-1-yl)borate
tetrakis(3-propylpyrazol-1-yl)borate
tetrakis(3-isopropylpyrazol-1-yl)borate
tetrakis(3-tert-butylpyrazol-1-yl)borate
tetrakis(3-neopentylpyrazol-1-yl)borate
tetrakis(3-phenylpyrazol-1-yl)borate
tetrakis(3-mesitylpyrazol-1-yl)borate
tetrakis(3-anisylpyrazol-1-yl)borate
tetrakis(3-m-tolylpyrazol-1-yl)borate
tetrakis(3-thienylpyrazol-1-yl)borate
tetrakis(3-naphthylpyrazol-1-yl)borate
tetrakis(3-anthracylpyrazol-1-yl)borate
tetrakis(3-fluorenylpyrazol-1-yl)borate
tetrakis(3,5-diphenylpyrazol-1-yl)borate
tetrakis(5-methyl-3-phenylpyrazol-1-yl)borate
tetrakis(3,5-di-isopropylpyrazol-1-yl)borate
tetrakis(camphorpyrazolyl)borate
tetrakis(2R,5R-menthylpyrazolyl)borate
tetrakis(indazol-2-yl)borate
tetrakis(2H-benz[G]indazol-2-yl)borate
tetrakis(4,5-dihydro-2H-benz[G]indazol-2-yl)borate
tetrakis(3-methyl-4,5-dihydro-2H-benz[G]indazol-2-yl)borate
tetrakis(1,4-dihydroindeno[1,2-c]pyrazol-1-yl)borate

hydridotris(3-propyl-9,9-dimethyl-4,5-diazatricyclo [6.1.0.$0^{2,6}$]non-2(6),3-dien-5-yl)borate
tetrakis(3-propyl-9,9-dimethyl-4,5-diazatricyclo [6.1.0.$0^{2,6}$]non-2(6),3-dien-5-yl)borate
hydridotris((7R)-4-propyl-7-(1-methyl-1-ethenyl)-2,3-diazabicyclo[3.3.0]oct-2-yl)borate
tetrakis((7R)-4-propyl-7-(1-methyl-1-ethenyl)-2,3-diazabicyclo[3.3.0]oct-2-yl)borate
hydridotris(7(R) or (S)-isopropyl-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate
hydridotris(pinanyl-pyrazolyl)borate
hydridotris(7(R) or (S)-tert.butyl-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate
hydridotris(7(R) or (S)-(1-methyl-1-phenylethyl)-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate
tetrakis(7(R) or (S)-isopropyl-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate
tetrakis(pinanyl-pyrazolyl)borate
tetrakis(7(R) or (S)-tert.butyl-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate and
tetrakis(7(R) or (S)-(1-methyl-1-phenylethyl)-4(R)-methyl-4,5,6,7-tetrahydro-indazol-2-yl)borate.

The remaining ligands or non-coordinating anions L may for example be any of the ligands conventionally used in organometallic olefin polymerization catalysts, e.g. aluminoxane (eg. MAO) residues, halide, alkyl or alkaryl such as halide, methyl and benzyl, as described in the above-referenced patent publications, as well as non-coordinating anions such as halogenates, perhalogenates, tetra-substituted borates (e.g. tetrafluoroborate, tetraphenylborate, tetrakis(p-fluorophenyl)borate, tetrakis(pentaphenyl)borate, tetratolylborate and tetraoctylborate), polyborates, tridecahydride-7-carbaundecaborate, bis(7,8-dicarbaundecaborate)cobaltate, group 15 halides (e.g. hexafluorophosphate), heteropolyanions, triflate, etc.

Tetra-substituted borates are preferred as non-coordinating anions.

The metal M which provides the catalytically active site in the catalysts of the invention is conveniently a lanthanide or actinide or a group 3, 4, 5, 6, 7, 8, 9 or 10 transition metal. Group 4 metals however are preferred, particularly titanium or hafnium and especially zirconium.

The use as olefin polymerization catalysts of pyrazolyl complexes of certain metals from groups other than group 4 is novel and forms a further aspect of the invention. Thus viewed from this aspect the invention provides a method of catalysed polymerization of an olefin using an olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said metal is selected from the actinides and lanthanides, Ta, Nb and the group 3, 7, 8, 9 and 10 transition metals, preferably a lanthanide or an actinide. In this method, the pyrazolyl group is either unsubstituted or substituted and preferably is 3-substituted as described above. If desired the pyrazolyl groups may carry no substituent or a methyl or ethyl substituent at the 3-position. Examples of such groups include (7R)-4-methyl-7-(1-methyl-1-ethenyl)-2,3-diazabicyclo[3.3.0]-oct-2-yl and 3,9,9-trimethyl-4,5-diazatricyclo[6.1.0.$0^{2,6}$]non-2(6),3-dien-5-yl group containing complexants. The preparation of the pyrazole starting materials for such catalysts is described by Popov et al in Tetrahedron: Asymmetry 5: 479(1994) and 6: 1013 (1995).

Viewed from a further aspect the invention also provides an olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said metal is selected from the actinides and lanthanides, Ta, Nb and the group 3, 7, 8,

9 and 10 transition metals, preferably a lanthanide or an actinide.

Viewed from a yet further aspect the invention provides a catalyst system comprising (i) a co-catalyst and (ii) an olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said metal is selected from the actinides and lanthanides, Ta, Nb and the group 3, 7, 8, 9 and 10 transition metals, preferably a lanthanide or an actinide.

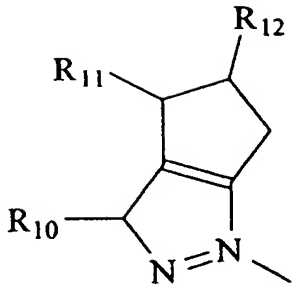
Viewed from a still further aspect, the invention comprises a catalyst system (and the use thereof in olefin polymerization) comprising a pyrazoyl-complex catalyst as defined above together with a further olefin polymerization catalyst, e.g. a heterogeneous or homogeneous catalyst such as a metal oxide or organometallic compound, optionally together with a co-catalyst.

The use of 4-substituted chiral 2,3-diazabicyclo [3.3.0]octan-2-yl and chiral 4, 5, 6 or 7 substituted indazol-2-yl complexants forms a further preferred aspect of the invention, i.e. the use of catalysts of formula II

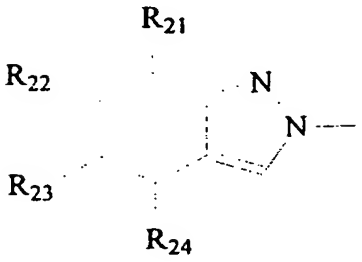
$$(Cx^1)_n(L)_mM$$

where n, m, M and L are as defined above and Cx^1 is a group Cx or a chiral 4-substituted-2,3-diazabicyclo[3.3.0]octan-2-yl or a chiral 4, 5, 6 or 7 substituted indazol-2-yl group, at least one Cx^1 being such a chiral group. Further aspects of the invention include catalyst systems involving catalysts of formula II analagous to those discussed above involving catalysts of formula I, and their use in olefin polymerization.

Chiral complexants Cx^1 are conveniently of formula IV or V

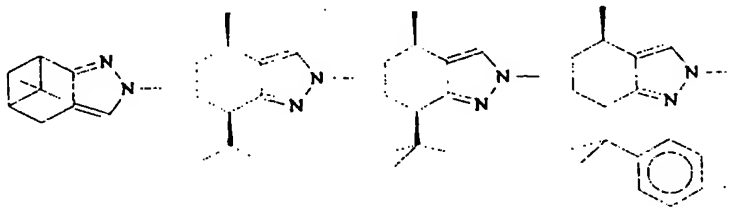


(IV)



(V)

where R_{10} is hydrogen, methyl, ethyl, a group R_3 or an R_4 substituted phenyl group; R_{11} and R_{12} are hydrogen or branched or linear optionally unsaturated alkyl (e.g. C_{1-6} alkyl or alkylene, e.g. propen-2-yl) or together form an optionally substituted 1 to 5 membered bridging group (e.g. a C_{1-5} alkandiyl group such as a propan-2,2-diyl group); and R_{21}, R_{22}, R_{23} and R_{24} are hydrogen, alkyl, or aralkyl or two non-adjacent such groups together from a bridging group, eg. a methylene or propan-2,2-diyl group. Suitable examples of Cx^1 include the chiral pyrazoles of Popov et al (supra) and the following indazol-2-yl groups:



eg. as described by Le Cloux et al. in JACS 115: 1153 (1993) and Organometallics 13: 2855 (1994).

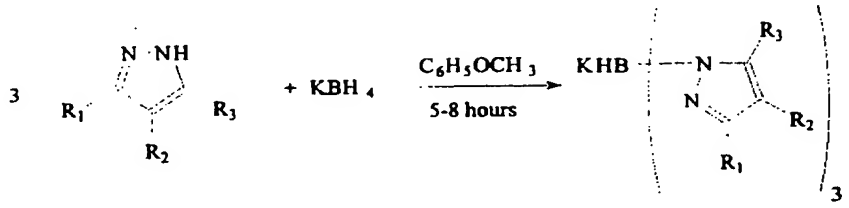
The 3-substituted-pyrazol-1-yl complexants Cx used in the production of the compounds of the invention may be prepared by conventional procedures, e.g. as described by Trofimenko in Chem Rev 93:943(1993). Ga, C, P and S linked multi pyrazolyl complexants Cz are described by Trofimenko in Prog. Inorg. Chem. 34: 115 (1986) and by Tokar et al. in Organometallics 11: 2737 (1992). Thus the complexants may conveniently be prepared by conjugating a corresponding 3-substituted-pyrazole to a backbone structure which provides group X. This process forms a further aspect of the present invention.

The backbone structure is conveniently an electrophile, such as a boron compound, and particularly preferably a borane or a metal borohydride. In general, tetrahydride compounds of group 13 metals, with group 1 metal counterions, can be used as the electrophile backbone structure. By regulating the temperature, solvent and reactant stoichiometry, the degree of substitution of the bridging group may be selected as desired. In general, temperatures between 50 and 200°C may be used and the progress of the substitution reaction can be followed by monitoring the volume of hydrogen evolved.

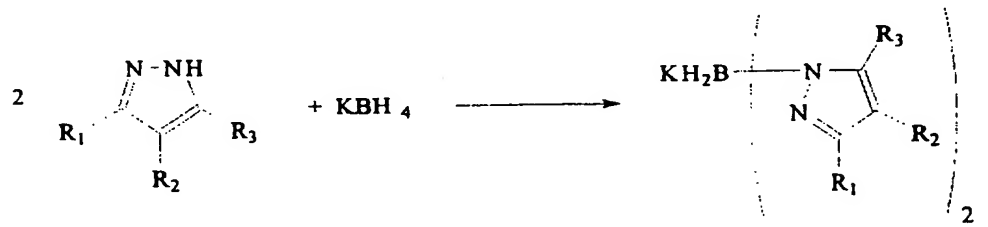
Other electrophiles, susceptible of nucleophilic substitution by the pyrazole or a pyrazolium ion may be used to produce different bridging groups X but the following illustrative discussion is limited to borane as an example of an appropriate bridging group former.

Mono, di, tri and tetra-pyrazol-1-yl borates may be prepared by reacting a metal borohydride such as KBH_4 with a pyrazole in the presence of a solvent or an excess of pyrazole. By control of the reaction conditions (e.g. temperature, stoichiometry, reaction time, etc) the degree of pyrazole substitution of the

boron can be regulated. Thus for example reaction of KBH_4 with three equivalents of pyrazole in a high boiling point solvent such as anisole yields a trispyrazolyl borate



while refluxing two equivalent of pyrazole with KBH_4 in N,N-dimethyl-acetamide yields the bispyrazolyl borate



(where R_1 is as described above and R_2 and R_3 are optional substituents on the 4 and 5 positions of the pyrazole).

Mixed trispyrazolyl borates can thus conveniently be produced by an initial disubstitution by refluxing with a first pyrazole in N,N dimethylacetamide followed by refluxing in anisole with a second pyrazole.

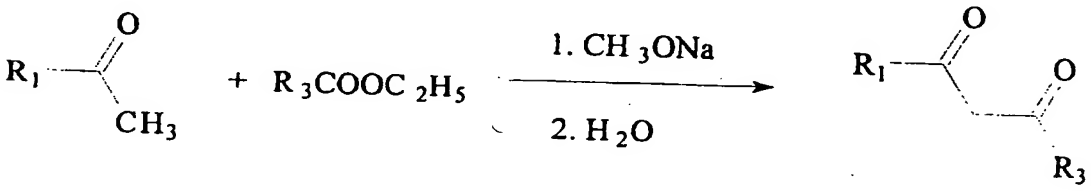
The preparation of pyrazolylborates is a known process and is described for example by Amoroso et al in J Chem Soc Chem Comm 2751(1994) and Trofimenko et al in Inorg Chem 33:3666(1994).

The novel 3-substituted pyrazoly-1-yl borates of formula $H_{4-p}B(Pz(R_1)_q)_p$ (where p is 2,3 or 4; each q is 0 or 1 with at least one being 1; Pz is a pyrazol-1-yl group and R_1 is as defined above) and the salts thereof form a further aspect of the present invention.

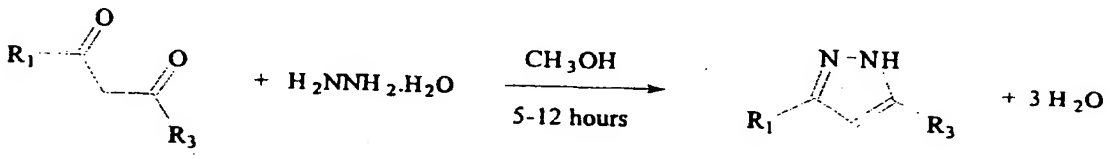
The 3-substituted pyrazoles used in the synthesis

of the pyrazolyl borates are either known compounds or may be prepared by procedures known from the literature.

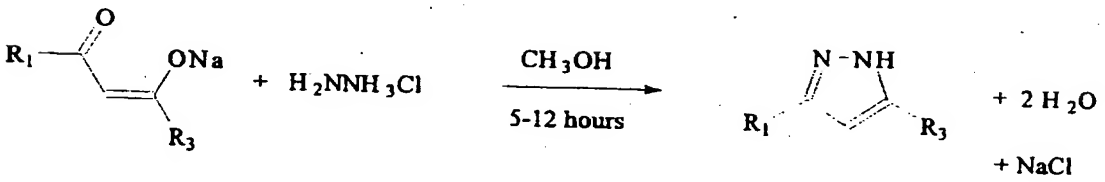
One particularly preferred method for the production of 3-substituted-pyrazoles involves ketone:carboxylate ester condensation to yield a diketone



followed by a cyclization using hydrazine

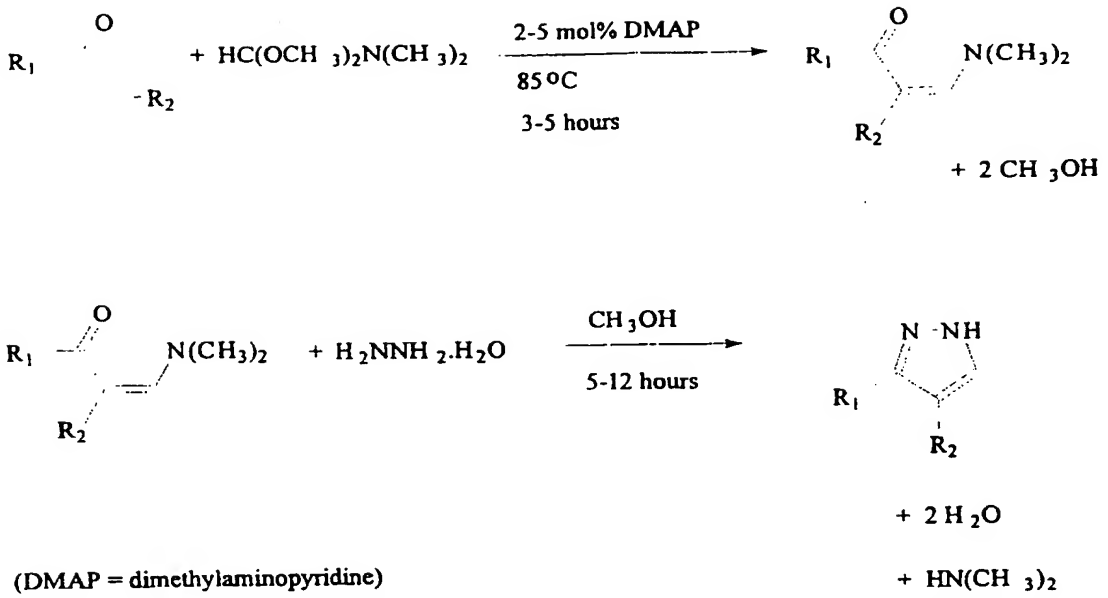


optionally performed using hydrazine hydrochloride and omitting hydrolysis of the enolate intermediate product of the diketone production reaction, i.e.



(see Trofimenko (1994) et al, supra).

Alternatively, 3-substituted pyrazoles can be prepared from ketones via carbonyl-enamines by reaction with N-dimethoxymethyl-N,N-dimethylamine followed by clyclization as above



(DMAP = dimethylaminopyridine)

This method (see Amoroso et al, supra) offers an attractive route to the 3,4-annelated pyrazoles.

The catalysts of the invention may be prepared by conventional techniques by reacting the complexant Cx with a compound of the metal, e.g. a chloride, bromide or iodide such as $TiCl_4$, $TiBr_4$, TiI_4, $ZrCl_4$, $ZrBr_4$ or ZrI_4 (especially preferably $TiCl_4$ or $ZrCl_4$). Compounds containing organic ligands L (e.g. methyl or benzyl) can be produced by reaction of the halide analog with a corresponding organometallic compound, e.g. methyllithium or benzylithium. Such techniques form a further aspect of the invention.

The catalyst compounds of the invention may be used as catalysts in olefin polymerization on their own or together with a co-catalyst (e.g. MAO or a cation activator) as described in the patent publications referred to above.

Preferably the co-catalyst is a Lewis acid that removes an organic ligand from the catalyst to yield a non-coordinating anion and a catalyst complex having an organic ligand which can serve for chain-initiation and an adjacent vacant coordination site. Where the catalyst has no organic ligands L available to serve as

chain-initiators, the co-catalyst desirably also serves to introduce such an organic group, e.g. by displacement of halide ions. Suitable co-catalysts include for example organoaluminium, organotin, organozinc compounds and borohydrides or boron halides.

Particularly preferably the co-catalyst is an organoaluminium compound, such as an alkylaluminoxane, or a cation producer (e.g. a compound of formulae XVI to XIX of EP-A-617052), and especially preferably it is the trimethylaluminium:water reaction product known as methylaluminoxane (MAO).

Such co-catalysts are used in conventional quantities relative to the pyrazolyl catalyst, eg. at from 1 to 10^8, preferably 1 to 10^4 moles aluminium per mole pyrazolyl-complexed metal, or 0.1 to 10 preferably 0.5 to 2 moles cation of cation producer per mole pyrazolyl-complexed metal. For MAO, the ratio of aluminium to catalytic metal (eg. Ti or Zr) may be very low, eg. 10:1 up to $1:10^8$. For other co-catalysts which form cations of the catalytic metal, stoichiometric ratios may be preferred.

The catalyst complexes of the invention may be used with or without a support. Heterogeneous catalysts comprising the catalyst compounds of the invention together with a substrate (ie carrier or support) form a further aspect of the invention. Examples of support or carrier materials include organic and inorganic materials, preferably in pulverulent form, eg. silica, carbon or a metal phosphate or oxide such as alumina, zirconia, titania or magnesium oxide. Catalyst loading levels on such supports will preferably be in the range 0.01 to 30% by weight. Examples of appropriate materials are discussed on page 37 of EP-A-617052. Inorganic supports, and especially predominantly porous silica supports (>90% by weight silica) are preferred. Since the catalyst will generally be retained in the polyolefin polymerization product, any inorganic carrier

material, and indeed the metallic components of the catalyst and any co-catalyst, should be selected with the end use of the polymer in mind and where the polymer is to be used for food storage, for example, toxic metals should be avoided.

The catalysts of the invention may be used for the polymerization of various olefins. Examples of suitable olefins include α-olefins such as ethylene, propylene, but-1-ene, pent-1-ene, 4-methyl-pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene and vinylcyclohexane; vinyl aromatics such as styrene and methyl-styrene; cyclic olefins such as cyclopentene, cyclohexene, cycloheptene and cyclooctene; conjugated dienes such as butadiene, cyclopentadiene and vinyl-1-cyclohexene; unconjugated dienes and polyenes; and alkynes, such as acetylene, butyne and hexyne. Alpha-olefins and alpha-diolefins having from 2 to 10 carbons, eg. ethylene, are preferred.

The catalyst can be used for copolymerization of two or more such olefin monomers. The catalyst can optionally be used together with a further olefin polymerization catalyst.

In a particularly preferred embodiment selective copolymerization may be effected using a 3-substituted-pyrazolyl catalyst according to the invention together with a further catalyst such as an inorganic metal oxide catalyst, a Ziegler-Natta type catalyst, or a coordination or organometallic catalyst in which the catalytically active site is not constricted by groups pendent from the organic complexant, e.g. complexes of tris 3-unsubstituted-pyrazolyl borate or Cp complexes. In this embodiment, copolymerization of a bulky monomer and a non-bulky monomer such as ethylene will give rise to a molecular aggregate of polymers having different (co)monomer compositions.

Furthermore, hydrogen can optionally be used as an adjuvant to the catalyst.

The polymerization can take place in conventional form, eg. in solution, slurry or in the gas phase, using for example slurry tank or loop reactors, fluidized bed or mechanically stirred bed reactors or in high pressure reactors above the melting point of the polymer.

Non-polymerizable organic solvents, such as alkanes or cycloalkanes may also be used as solvents for the reaction. The reaction temperature may be reduced, ambient or elevated. Temperatures of -50 to 300°C, preferably 50°C to 250°C may be used as may be pressures of 1 to 2000kg/cm^2 G.

A preferred polymerization technique is the slurry process in which the temperature is kept below the temperature at which the polymer product dissolves in the reaction solution. For slurry polymerization, reaction temperatures of 50-110°C, preferably 60 to 105°C, are conveniently used. The pyrazolyl-complexed catalyst is used in catalytic quantities.

The invention will now be illustrated further by the following non-limiting Examples:

In these Examples, molecular weight and GPC curves were determined using a Waters 150 CV instrument operating with Waters Expert Ease software. Calibration was effected according to SECV PS (Polymer Lab) Narrow standard calibration: column set: 3 x Waters, Linear, Styragel High Temperature, 7.8 x 300 mL. The analyses were run at 140°C with trichlorobenzene (TCB) and 0.25 g/L 2-tert.butyl-4-methylphenol as solvent. The sample concentration was about 0.0005 g_{sample}/g_{TCB} with an injection volume of 500 μL. The dissolution conditions were: 2 hours 140°C + 4 hours 160°C + 4 hours 140°C (atmosphere:air; filtration by inline filter only).

EXAMPLE 1

3,5-Diphenylpyrazole

In a 2L reaction vessel equipped with mechanical

stirrer, cooler and bromine addition ampoule, 0.1mol of 1,3-diphenylpropan-1,3-dione is dissolved in 90mL methanol. The solution is cooled on an ice bath and 0.11mol hydrazine hydrate solution in methanol is added. Once the reaction is finished, the solution is refluxed for 5 to 12 hours. The solvent is evaporated off and the title compound is purified by recrystallization from acetone.

Yield: 90%. MPt > 250°C.

^{1}H NMR (200 MHz, CD_3COCD_3): δ 4.97 (s br, NH), 6.99 (s, 1H), 7.35-7.50 (m, $6H_{arom}$), 7.73-7.78 (m, $2H_{arom}$).

^{13}C NMR (50.25 MHz, CD_3COCD_3): δ 102.7 (CH), 126.1 (2 CH), 128.4 (CH), 128.9 (2 CH), 131.3 (C), 133.4 (CH), 148.6 (C).

The following pyrazoles are produced analogously:

(1) 3,5-dimethylpyrazole

Starting material: 2,4-pentadione. Product purified by sublimation. T_s=84°C at 9.10^{-3}mbar. MPt 105°C.

Yield: 95%.

^{1}H NMR (200MHz, $CDCl_3$): δ 2.28 (s, 6H), 5.82 (s, 1H), 9.10-10.12 (s br, NH).

^{13}C NMR (200MHz, $CDCl_3$): δ 12.2 (2CH), 104.0 (CH), 144.1 (2C).

(2) 5-methyl-3-phenylpyrazole

Starting material: 1-phenyl-1,3-butadione. Product purified by sublimation. T_s=132°C at 8.10^{-3}mbar. MPt 123°C.

Yield: 94%.

^{1}H NMR (200MHz, $CDCl_3$):δ 2.32 (s, 3H), 6.36 (s, 1H), 7.27-7.43 (m, $3H_{arom}$), 7.70-7.75 (m, $2H_{arom}$).

^{13}C NMR (50.25MHz, $CDCl_3$):δ 11.7 (CH), 125.8 (2CH), 127.8 (CH), 128.7 (2CH), 144.5 (C).

(3) 3-t-butylpyrazole

Starting material: 2,2 dimethyl-3,5-pentadione. Product purified by distillation. Boiling point 72-80°C at 10^{-1}mbar. MPt 38°C.

Yield: 52%.

^{1}H NMR (100MHz, $CDCl_3$):δ 1.35 (s, 9H), 6.09 (d, J=2.0Hz, 1H), 7.45 (d, J=2.0Hz, 1H).

^{13}C NMR (25.13MHz, $CDCl_3$):δ 30.6 ($3CH_3$), 101.1 (CH), 135.7 (CH), 156.0 (C).

(4) 3-phenylpyrazole

Starting material 1-phenyl-1,3-propandione. Product purified by distillation. Boiling point 128°C at 10^{-2}mbar. MPt 83°C.

Yield: 65%.

^{1}H NMR (200MHz, $CDCl_3$): δ 6.57 (d(J=2.2Hz), 1H), 7.27-7.43 (m, $3H_{arom}$), 7.58 (d(J=2.2Hz), 1H), 7.68-7.80 (m, $2H_{arom}$), 13.32 (m, $1H_{N-H}$).

^{13}C NMR (50.25MHz, $CDCl_3$):δ 102.7 (CH), 126.0 (2CH), 128.4 (CH), 128.9 (2CH), 133.4 (C), 148.6 (C).

EXAMPLE 2

Potassium bis hydrido bis(3'-phenyl-pyrazol-1-yl)borate

Into a 1L reactor equipped with a magnetic stirrer bar, a cooler and an oil bubbler connected to a graduated expansion vessel is introduced 0.24mol of 3-phenyl-pyrazole and 20mL of freshly distilled N,N-dimethylacetamide. 0.11mol KBH_4 is introduced in one portion and the heterogeneous mixture is placed in a bath at 170°C. The progression of the reaction is followed by measuring the volume of hydrogen evolved. After 6 hours' heating, 5L of hydrogen have been evolved and the solvent is distilled off in vacuo. The viscous solid residue is suspended in hot toluene. The white solid which remains is filtered and washed repeatedly with toluene, then pentane, then dried under reduced pressure.

Yield 60%. (38g, 0.11mol) white solid.

Disubstitution is verified by the presence of a characteristic BH_2 doublet in the IR spectrum at 2367 and 2347cm^{-1}.

EXAMPLE 3

Potassium hydrido tris (3'-phenylpyrazol-1-yl)borate

Into a 250mL twin necked flask is introduced 6.76g (0.02mol) of the bispyrazolyl complex of Example 2 and 100mL anisole. 2.88g (0.02mol) 5-phenylpyrazole is added. The mixture is refluxed for 6 hours and then allowed to cool to ambient temperature. The solid in suspension is filtered, repeatedly washed with hot toluene and with pentane, and dried under reduced pressure. Trisubstitution is verified by the disappearance of the IR doublet and the appearance of a BH singlet at 2417cm^{-1}.
Yield: 54%, 5.2g white solid.

EXAMPLE 4

Potassium bis hydrido bis(3,5-dimethyl-pyrazol-1-yl) borate

In a 250mL flask, 21.2g (0.22mol) of 3,5-dimethyl-pyrazole and 5.395g (1eq) of KBH_4 are dissolved in dimethyl acetamide (DMAC). The mixture is heated at 150-180°C for about 5 hours by which time hydrogen evolution has ceased. The mixture is cooled and the white solid which forms is separated by filtration and washed with hot toluene.
Yield: 9.7g (40%), white solid.

The following compound is produced analogously:

(1) Potassium bishydrido bis(5-methyl-3-phenyl-pyrazol-1-yl)borate

Starting materials 0.2mol 5-methyl-3-phenyl-pyrazole, 0.1mol KBH_4 and 140mL DMAC.
Yield: 35%.

EXAMPLE 5

Potassium hydrido tris(3,5-dimethyl-pyrazol-1-yl)borate

In a 150mL flask, 9.42g (0.0389mol) of the compound of Example 4 and 3.74g (1eq) of 3,5-dimethylpyrazole are dissolved in 90mL anisole. The mixture is stirred at 170°C for 12 hours. After cooling on an ice bath, a white precipitate forms which is isolated by filtration and washed with toluene and hexane. The white solid is then dried in vacuo.

Yield: 6.7g (51%)

The following compound is produced analogously:

(1) Potassium hydrido tris(5-methyl-3-phenyl-pyrazol-1-yl)borate

Starting materials 0.0335mol compound of Example 4(1), 0.0335mol 5-methyl-3-phenyl pyrazole and 100mL anisole. Yield: ca. 5g (ca. 30%).

EXAMPLE 6

$HB(3\text{-}Ph\text{-}5\text{-}Me\text{-}Pz)_3TiCl_3$ (Hydrido(3-phenyl-5-methyl-pyrazol-1-yl)borate:titanium chloride)

Potassium hydrido tris(3-phenyl-5-methyl-pyrazol-1-yl)borate (0.500g, 0.957mmol) is dissolved in 25mL THF and cooled to 0°C. To the cooled solution is added a small excess of $TiCl_4$ (> 0.1mL). The resulting yellow solution is refluxed overnight during which a colour change to red-brown occurs. The THF is evaporated off and the product is dissolved in 10mL toluene. This solution is used for the polymerization experiments reported below. With the addition of 3mL heptane a white precipitate (KCl) forms.

EXAMPLE 7

HB(Pz)$_3$TiCl$_3$(Hydrido(pyrazol-1-yl)borate:titanium chloride)

The title compound may be prepared by the method of Kouba et al, Inorg Chem 15:2313(1976).

5.18g (20.6mmol) of potassium hydrido tris pyrazol-1-yl borate is dissolved in 100mL of tetrahydrofuran (THF) and the solution is cooled to 0°C. To the cooled solution, 2.30mL (20.6mmol) $TiCl_4$ is added dropwise and the resulting yellow suspension is refluxed for 12 hours. The yellow solid formed is isolated by filtration, dried in vacuo and sublimed onto a water-cooled probe.
Yield: 3.99g (10.9mmol, 53%) fine yellow-orange needles.

EXAMPLE 8

HB(3,5-Me$_2$ Pz)$_3$ TiCl$_3$(Hydrido(3,5-dimethyl-pyrazol-1-yl)borate:titanium chloride)

Potassium hydrido tris(3,5-dimethyl-pyrazol-1-yl) borate (0.400g, 1.23mmol) is dissolved in 20mL THF and cooled to 0°C. To the cooled solution is added a small excess of $TiCl_4$ (ca. 0.15mL). The resulting yellow solution is refluxed overnight during which a colour change to orange occurs. The THF is evaporated off and the product is dissolved in 30mL toluene and filtered. This solution is used in the polymerization experiments reported below.

EXAMPLES 9 - 13

Polymerization tests were performed in a 200ml glass reactor with a heating/cooling jacket, magnetic stirring, a stainless steel thermocouple and a sceptre. The temperature was kept within ±1°C by circulating water from a thermostated reservoir. In a typical polymerization test, the reactor was first evacuated and

filled with argon gas. Then toluene was added. When the reactor temperature was constant at the desired temperature, a toluene solution containing the desired amount of the metal complex was added using a syringe. The argon was flushed away and replaced by ethylene. A toluene solution of methylaluminoxane (MAO from AKZO) was added as the last component. During the polymerization, the ethylene pressure in the reactor was kept constant at approximately 1 atmosphere by continuously adding ethylene through a mass-flow meter. The amount of ethylene consumed per unit time and the temperature in the reactor could be monitored and sampled on a computer. If desired, a certain amount of argon could be added to the reactor to keep the ethylene pressure lower than 1 atmosphere, or a desired pressure of hydrogen could be added. In some tests, 1ml of 1-hexene was added to the toluene as a co-monomer before the catalyst components were added. At the end of the polymerization, the ethylene flow was closed, the reactor flushed with argon, the catalyst destroyed and the polymer precipitated by adding acidic methanol (1% HCl in methanol). The polymer was filtered off, washed with methanol and dried in a heating cupboard at 60°C overnight.

EXAMPLE 9

Polymerization of ethylene using ($HB(Pz)_3$ $TiCl_3$) and MAO

Two 200mL glass reactors each containing 30mL toluene under an argon atmosphere are charged with 25mL and 16.7mL respectively of a slurry of $HB(Pz)_3$ $TiCl_3$ in toluene (containing 50mg (0.136mmol) and 36mg (0.098mmol) $HB(Pz)_3$ $TiCl_3$ respectively). Argon is removed and replaced by ethylene by repeated evacuation. 10.0mL and 3.6mL respectively of a solution of MAO (available from AKZO) in toluene are added to the reactors providing Al/Ti ratios of 173 and 87

respectively. Ethylene is added to the reactors to maintain pressure constant at about 1 atmosphere during the polymerization reaction. The reactor temperature is maintained constant at 50°C using a thermostatted bath. After one hour polymerization time, the polymer is precipitated by the addition of methanolic HCl. The precipitate is filtered and dried at 60°C.

Yield: reactor 1 - 262mg polymer
reactor 2 - 289mg polymer.

The molecular weight distribution of the product of reactor 2 is determined by gel permeation chromatography(GPC) and the GPC curve is shown in Figure 1A of the accompanying drawings.

EXAMPLE 10

Polymerization of ethylene using $HB(3,5\text{-}Me_2\text{-}Pz)_3TiCl_3$ and MAO

The procedure of Example 9 is repeated using 50mg (0.114mmol) of $HB(3,5\text{-}Me_2\text{-}Pz)_3TiCl_3$ and MAO at an Al/Ti ratio of 84 with the further addition of 1ml 1-hexene in reactor 2. The polymerization was run for 1 hour at 30°C.

Yield: reactor 1 - 1.325g polymer
reactor 2 - 1.051g polymer.

The GPC curve for the product of reactor 1 is shown in Figure 1B of the accompanying drawings.

EXAMPLE 11

Polymerization of ethylene using $HB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_3TiCl_3$ and MAO

Two 200mL glass reactors each containing 50mL toluene under an argon atmosphere are each charged with 1mL of a slurry of $HB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_3TiCl_3$ in toluene

containing 61mg (0.0957mmol) of $HB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_3TiCl_3$. Argon is removed and replaced by ethylene by repeated evacuation. 3.0mL of a solution of MAO in toluene is added to each reactor to provide an Al/Ti ratio of 92. Ethylene is added to the reactors to maintain present constant at about 1 atmosphere during the polymerization reaction. The reactor temperatures are maintained constant at 50°C (reactor 1) and 31°C (reactor 2) using thermostatted baths. After one hour polymerization time, the polymer is precipitated by addition of methanolic HCl. The precipitates are filtered and dried at 60°C.

Yield: reactor 1 - 302mg polymer
reactor 2 - 501mg polymer.

The molecular weight distribution of the product of reactor 1 is determined by GPC and the GPC curve is shown in Figure 1C of the accompanying drawings.

From Figure 1 it is evident that substitution of the pyrazolyl group allows a modification of the molecular weight distribution, in particular producing a relatively higher proportion of high molecular weight product.

EXAMPLE 12 (COMPARATIVE)

Polymerization with $HB(Pz)_3CrCl_2(pyr)$

$KHB(Pz)_3$ (0.3g, 1.1899mmol) was added to a slurry of $CrCl_3(THF)_3$ (0.44g, 1.1743mmol) in THF (25ml) at ambient temperature. The reaction mixture was stirred for 0.5 hours. Pyridine (1.0ml, 12.36mmol) was added and the mixture refluxed overnight. THF was removed under reduced pressure and the complex was dissolved in acetone (15ml). The catalyst was prepared by using 1ml of the acetone solution, removing the acetone under

reduced pressure and adding 16.28ml MAO in toluene (AKZO) to the solid residue to achieve a Al/Cr ratio of 400. This mixture was stirred for 15 minutes before 8ml of the solution was added to each polymerization reactor together with 45ml toluene. The polymerizations were performed at 30°C (reactor 1) and 60°C (reactor 2)under atmospheric ethylene pressure. After 2 hours and 10 minutes polymerization time, 0.080 and 0.005g polyethylene could be precipitated with methanolic HCl from reactors 1 and 2 respectively.

EXAMPLE 13

Polymerization with $HB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_3CrCl_2$

$KHB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_3$ (0.178g, 0.3705mmol) was added to a slurry of $CrCl_3(THF)_3$ (0.140g, 0.3737mmol) in THF (10ml) at ambient temperature. The reaction mixture was stirred for 20 minutes. THF was removed under reduced pressure and 25ml toluene was added. The catalyst was prepared by reacting 4ml of the toluene suspension with 10ml MAO/toluene at ambient temperature for 10 minutes. 2.5ml of the catalyst solution was used in polymerization tests at 30°C (reactor 1) and 60°C (reactor 2). After 1 hour and 15 minutes polymerization time, 0.220 and 0.012g polyethylene could be precipitated with methanolic HCl from reactors 1 and 2 respectively.

EXAMPLE 14

Solid Phase Catalyst

10g silica of the type Crossfield EP-10 is calcined at 500°C for 10 hours with nitrogen. The silica is cooled under nitrogen and the pore volume is checked to be in the range 1.6-2 ml/g. All of the following operations are performed under an argon atmosphere in a

glove box: a solution of MAO/catalyst is prepared according to one of the earlier examples (e.g. Example 9) 0.196 mmol of a hydridotrispyrazolyl : $TiCl_3$ catalyst being dissolved in 13 ml toluene and combined with 7.2 ml MAO in toluene, giving a solution with an Al/Ti ratio of 87. 2 ml of this solution is added to 1g calcined EP-10 in a septum bottle while stirring with a magnetic stirring bar. The silica initially clumps together and regains its free flowing properties after stirring for a while. Inert gas is bubbled through the thus prepared catalyst for 1 hour using a thin needle and continually stirring the powder. The catalyst is now ready for use.

EXAMPLE 15

HB(3-Me-5-Phenyl-Pz)$_3$ $ZrCl_3$

0.76 mmole of $ZrCl_4$ (0.178g) was dissolved in a mixture of 30ml methylene chloride and 15 ml diethylether at -78°C. 0.76 mmole potassium (bis-hydrogen, bis(3-methyl-5-phenyl-pyrazole)borate) (0.280g) was added and the reaction mixture was slowly raised to ambient temperature overnight. A white precipitate was filtered off, the solvent removed under reduced pressure leaving a white powder. The NMR data is consistent with the title product.

All NMR shifts in PPM with respect to TMS. Solvents used as internal standards.

^{1}H-NMR; d_8-THF

δ2.69(s)	C(5)-C<u>H</u>$_3$	Pz
δ6.94(s)	C(4)-<u>H</u>	Pz
δ7.56-7.64(m),8.31-8.36(m)	C-<u>H</u>	Ph

^{13}C-NMR; d_8-THF

δ13.2	C(5)-$\underline{C}H_3$	Pz
δ105.9	C(4)	Pz
δ128.5, 130.2, 131.5		Ph
δ147.7, 150.0	C(3),C(5)	Pz

EXAMPLE 16

Polymerization with $HB(3\text{-Me-5-Phenyl-Pz})_2\ ZrCl_3$

A polymerization test was performed with 0.048 mmole of the complex of Example 15 in 50 ml toluene using MAO as cocatalyst (Al/Zr = 200). The test was performed at 30°C under 1 atmosphere of ethylene. After 139 minutes the polymerisation was stopped and the polymer was precipitated by adding a hydrogen chloride-methanol mixture. Yield of polyethylene: 0.853g, corresponding to a productivity of 86 g PE/mmol Zr hr^{-1}.

EXAMPLE 17

$H_2B\ (N_2C_3H(C_8H_8))_2\ ZrCl_3\ THF$

305 mg (1.33 mmole) $ZrCl_4$ was suspended in 30 ml methylene chloride, cooled to -78°C and 15 ml of diethylether was added dropwise. 517 mg (1.33 mmole) $H_2B(N_2C_3H(C_8H_8))_2K$ (prepared as described in Example 21) was added as a dry powder. The resulting slurry was then slowly warmed to ambient temperature resulting in a clear solution. The reaction was continued for 3 days resulting in a clear light yellow solution. The solvent mixture was removed under reduced pressure. The off-white residue was dissolved in 25 ml THF and stirred at ambient temperature overnight. The white precipitate (KCl) was filtered off on a G-4 fritt and the THF removed under reduced pressure. The product gives elemental analysis in accordance with the title product.

Elemental analyses: Found: C 49.9%, H 8.5%, N 4.7%, Calculated: C 50.3%, H 9.0%, N 4.5%.

All NMR shifts in PPM with respect to TMS. Solvents used as internal standards.

^{1}H-NMR: CD_2Cl_2

δ1.17(t), 3.45(t)		THF
δ2.78(t), 2.96(t)	$C\underline{H}_2C\underline{H}_2$	Tetralone
δ7.2-8.2(m)	C(aromatic)	Pz+Tetralone

^{13}C-NMR: CD_2Cl_2

δ15.3, 65.9		THF
δ18.7, 29.0	$\underline{C}H_2\underline{C}H_2$	Tetralone
δ118.0(br), 123.8(br), 127.4,129.2, 130.4(br), 138.2, 142.0(br)	C(aromatic)	Pz+Tetralone

EXAMPLE 18

Polymerization with $H_2B(N_2C_3H(C_8H_8))_2ZrCl_3.THF$

Polymerization was performed as described for Examples 9-13. Running the polymerization with 0.05 mmole of the complex of Example 17 together with 4.2 ml MAO in 50 ml toluene for 159 minutes at 30°C and 1 atmosphere ethylene pressure results in 1.47g polyethylene. This corresponds to a productivity of 122g PE/mmole Zr hr^{-1}.

EXAMPLE 19

$H_2B(3\text{-mesityl-Pz})_2ZrCl_2(C_5H_5)$

The title complex was synthesized using a method similar to that of Reger et al., Inorg. Chem. 25: 2046 (1986) using, however, as the starting material $(C_5H_5)ZrCl_3$ and not the DME adduct. $(C_5H_5)ZrCl_3$(100 mg, 0.381 mmole) and potassium (bis-hydrogen, bis(3-mesityl-pyrazole) borate) (160 mg, 0.379 mmole) was added to 10 ml methylene chloride at -78°C. The reaction mixture was filtered

and all volatiles removed under reduced pressure at -10°C, resulting in pale brown crystals. The NMR data are in accordance with the title product.

All NMR shifts in PPM with respect to TMS. Solvents used as internal standards.

^{1}H-NMR; CD_2Cl_2

δ2.02(s),2.04(s)	CH_3	2,6-Mes
δ2.31(s)	CH_3	4-Mes
δ6.12(s,br),6.37(s,br)	C(4)-H	Pz
δ6.61(s)		Cp
δ6.92-6.96(m)	C(3)-H,C(5)-H	Mes
δ7.71(s,br),8.16(s,br)	C(5)-H	Pz

^{13}C-NMR; CD_2Cl_2

δ20.3	CH_3	2,6-Mes
δ21.0	CH_3	4-Mes
δ106.4,108.4	C(4)	Pz
δ119.8		Cp
δ124.5,126.1,128.5,128.7,137.5, 137.8,139.4,140.0	C(aromatic)	Mes
δ141.2,141.8,143.4,143.5	C(3),C(5)	Pz

EXAMPLE 20

Polymerization with $H_2B(3\text{-mesityl-Pz})_2\ ZrCl_2(C_5H_5)$

The complex of Example 19 (75 mg, 0.123 mmole) was added to 10.6 ml MAO (Al/Zr = 200) and stirred for 10 minutes. The catalyst mixture was added to toluene (45 ml at a pre-set temperature) in the reactor by use of a syringe. After 85 minutes 1g polymer was collected. This corresponds to a productivity of 156gPE/mmole Zr hr^{-1}.

EXAMPLE 21

$H_2B(N_2C_3H(C_8H_8))_2K$

Formyl tetralone was synthesized by processes (A) or (B) below:

(A) Metallic Na (3.3 g, 0.14 mol) is cut into small pieces and suspended in 2 L of absolute ethyl ether. This suspension is vigorously stirred and 0.1368 mol of α-tetralone and 0.205 mol of ethylformate. The exothermic reaction is started by the addition of 0.6 mL of anhydrous ethanol and cooled by means of an ice bath. After 10 hours 10 mL of ethanol are added and the mixture is stirred one more hour. Water is added and the biphasic mixture is stirred for some minutes before being separated. The organic layer is washed with water and the combined aqueous phases are extracted with ether. The aqueous phase is acidified with 6N HCl and extracted with ether. The combined organic phases are washed with a saturated solution of NaCl, dried ($MgSO_4$) and filtered. Removal of the solvent in vacuo afforded the crude product, formyl tetralone, which is purified by distillation (bp 90°C/12mm Hg). Yield 20.2g (85%).

(B) Sodium hydride (14g, 0.35 mol) is separated from paraffin by repetitive washings (3 times) with hexane and suspended in freshly distilled dry THF (1 mol/L). The mixture is placed under nitrogen and cooled to 0°C before ethyl formate (30 mL, 0.37 mol) is added with stirring. After 10 minutes, α-tetralone (20g, 0.1368 mol) is slowly added (diluted with dry THF). After 10 more minutes, the mixture is warmed to room temperature and stirred one night. The mixture is acidified at 0°C with acetic acid (pH 5). The phases are separated and the aqueous phase is extracted 3 times with ether.

The combined organic phases are washed with a saturated solution of NaCl, dried ($MgSO_4$) and filtered. Removal of the solvent in vacuo afforded the crude product, formyl tetralone, which is purified by distillation (bp 90°C/12 mm Hg). Yield 19.9g (84%).

The formyl tetralone was then reacted with hydrazine to yield tetralonepyrazole as follows:

(C) A solution of the formyl tetralone (40g, 0.23 mol) in methanol is placed in a round-bottomed flask equipped with a reflux condenser. Hydrazine hydrate (11.6 mL, 0.234 mol) is added over a period of 10 minutes. The reaction is exothermic and may require temperature control with an ice bath. After 20 minutes the reaction mixture is heated to reflux during 4 hours. After cooling, methanol is evaporated and the residual pyrazole is dissolved in chloroform. The organic phase is dried ($MgSO_4$) and filtered. Removal of the solvent in vacuo afforded the crude α tetralone-pyrazole which is dried (high vacuum pump) and eventually sublimed yielding the tetralone pyrazole as white powder. Yield 33.4g (85%) —
^1H NMR ($CDCl_3$) δ2.82 (m, 2H); 2.94 (m, 2H); 7.23 (m, $4H_{arom}$); 7.39 (s, 1H); 7.75 ppm (m, 1H).

$H_2B(N_2C_3H(C_8H_8))_2K$ was then synthesized from the tetralonepyrazole by the procedure of Rheingold et al, Inorg. Chem. 33: 3666 (1994) using 12g (0.0305 mol) tetralone pyrazole, 1.99g (0.0355 mol) KBH_4 and 20 mL DMAC. Purification by sublimation (Kugelrohr) yielded 2.2 g (16%) of the potassium compound.

^1H NMR (DMSO d_6): δ 2.67 (m, 2H); 2.85 (m, 2H); 7.1-7.3 (m, 3H); 7.50 (bs, 1H); 7.64 ppm (bs, 1H)

^{13}C NMR (DMSO d_6): δ 18.74; 29.22; 121.37; 126.59; 126.99; 128.36 ppm.

EXAMPLE 22

$HB(5\text{-}Me\text{-}3\text{-}Ph\text{-}Pz)_2ZrCl_2(C_5H_5)$

The title complex was prepared analogously to that of Example 19 using $(C_5H_5)ZrCl_3$ and potassium (bis-hydrogen, bis(3-methyl-5-phenyl-pyrazole) borate).

EXAMPLE 23

Heterogeneous catalyst

To SiO_2 calcined at 400°C was added 2.48 ml of a heptane solution containing 0.080 g MAO such that the pores of the silica were filled. The mixture was stirred for 0.5 hr., then the heptane was removed under reduced pressure. 10mg of the complex of Example 22 dissolved in 4 ml CH_2Cl_2 was then added and the mixture was stirred for 1 hr. CH_2Cl_2 was removed under reduced pressure leaving a dry powder. Polymerization with 400 mg of the heterogenized catalyst at 80°C with approximately 20 bar ethylene in 0,5l isobutane for 60 minutes gave 6 g polyethylene, corresponding to an activity of 683 gPE/mmoleZr/hr.

Claims:

1. An olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said complexant contains a pyrazol-1-yl group substituted in the 3-position by an organic moiety containing at least 3 carbon atoms.

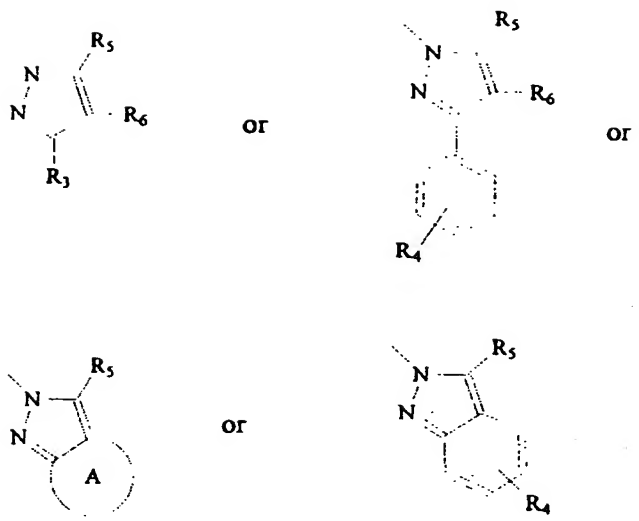
2. A compound as claimed in claim 1 wherein said moiety comprises a C_{3-20} alkyl group, an optionally substituted aryl group or an optionally substituted bridging moiety creating a 5 to 9 membered carbocyclic ring joined at the 3 and 4 positions.

3. A catalyst compound as claimed in either of claims 1 and 2 of formula I

$$(Cx)_n(L)_mM \qquad (I)$$

(where M is a transition metal, lanthanide or actinide; L is a mono or polydentate ligand or a mono or polyvalent non-coordinating anion; Cx is a mono or polydentate organic complexant comprising a 3-substituted pyrazol-1-yl group; n is a positive integer; and m is zero or a positive integer), or a salt thereof.

4. A compound as claimed in claim 3 comprising a Cx group of formula



where R_3 is a linear or branched C_{3-8} alkyl group, R_4 is hydrogen alkyl, aryl, fused aryl or COOH or SO_3H (or a salt, ester or amide thereof), R_5 is hydrogen or optionally substituted alkyl or aryl, R_6 is a hydrogen or halogen atom or an alkyl, aryl or aralkyl group, and A is a C_5 or C_6 ring optionally carrying a further 4 to 6 membered fused ring and optionally substituted by R_4 or by alkyl or alkaryl groups.

5. An olefin polymerization catalyst compound of formula III

$$(Cx^1)_n(L)_mM$$

where n, m, M and L are as defined in claim 3 and Cx^1 is a group Cx as defined in claim 3 or claim 4 or a chiral 4-substituted-2,3-diazabicyclo[3.3.0]octan-2-yl or a chiral 4, 5, 6 or 7 substituted indazol-2-yl group, at least one Cx^1 being such a chiral group.

6. A catalyst compound as claimed in any one of claims 1 to 5 comprising at least one complexant group Cx of formula II

$X(Pz(R_1)_q)_p$ (II)

(where q is 0 or 1, at least one q being 1; p is 1, 2, 3 or 4; R_1 is an organic group containing at least three carbons and attached to Pz at the 3-position; and X is an organic group containing at least 3 carbons or a bridging group linking two or more pyrazol-1-yl moieties) or a salt thereof.

7. A catalyst compound as claimed in any one of claims 1 to 6 comprising at least one 3-substituted pyrazol-1-yl complexant group wherein the 3-substituent is an optionally substituted alkyl, aryl or aralkyl group.

8. A catalyst compound as claimed in any one of claims 1 to 7 being a zirconium complex.

9. An olefin polymerization catalyst compound comprising a catalytically effective metal complexed by a pyrazol-1-yl group containing complexant, characterised in that said metal is selected from the actinides and lanthanides, Ta, Nb and the group 3, 7, 8, 9 and 10 transition metals.

10. A compound of formula $H_{4-p}B(Pz(R_1)_q)_p$ (where p is 2, 3 or 4; each q is 0 or 1 with at least one q being 1; Pz is a pyrazol-1-yl group; and R_1 is an organic group containing at least three carbons and attached to Pz at the 3-position) or a metal complex or salt thereof.

11. A compound as claimed in either of claims 9 and 10 comprising a 3-substituted pyrazol-1-yl group as defined in any one of claims 2, 4 and 5.

12. A catalyst system comprising (a) a catalyst compound and (b) a co-catalyst, wherein said catalyst compound is a compound as claimed in any one of claims 1

to 9.

13. A catalyst system as claimed in claim 12 wherein said co-catalyst is a cation complex forming activator.

14. A catalyst system as claimed in claim 13 wherein said activator is reactive with said catalyst compound to yield an organometallic cation and a non-coordinating anion.

15. A catalyst system as claimed in claim 12 wherein said co-catalyst is an alkylaluminoxane.

16. A heterogeneous catalyst comprising a catalyst compound or system as claimed in any one of claims 1 to 15 and a porous substrate.

17. A heterogeneous catalyst as claimed in claim 16 wherein said substrate is silica.

18. A process for catalysed polymerisation of olefins, characterised in that as a catalyst is used a catalyst or catalyst system as claimed in any one of the preceding claims.

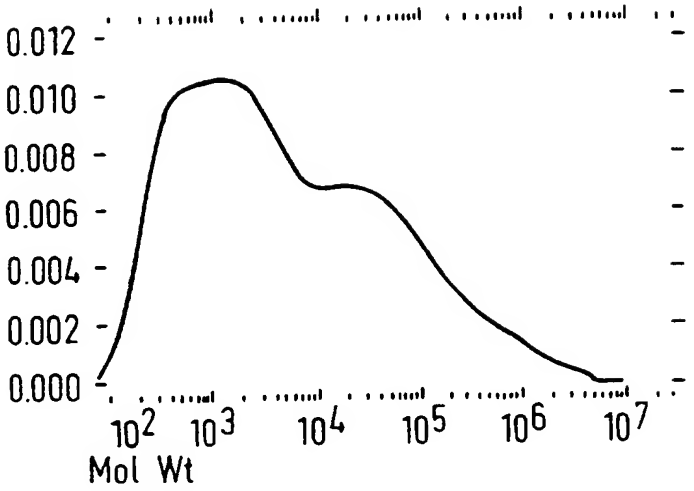


FIG. 1A

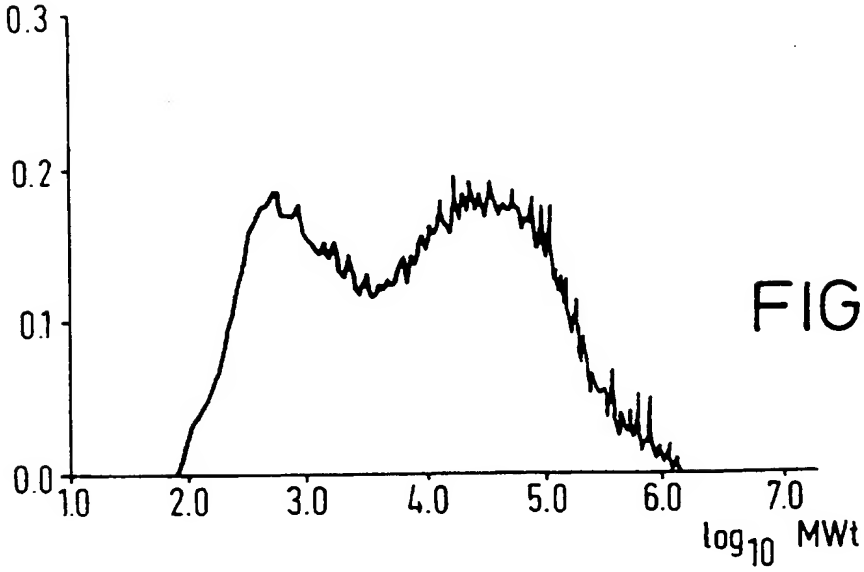


FIG. 1B

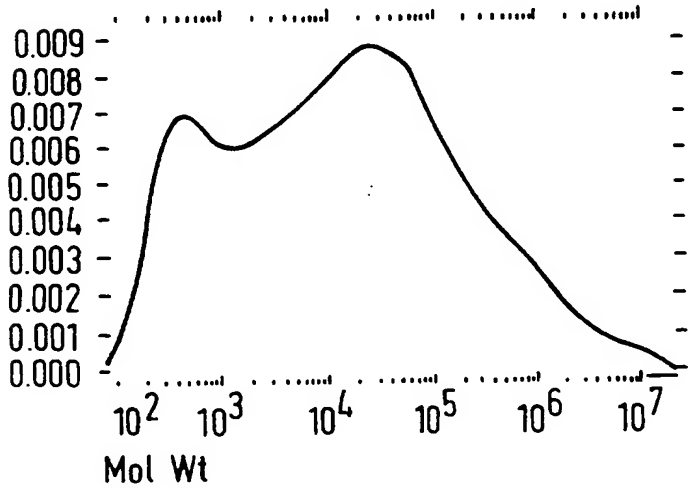


FIG. 1C

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/GB 96/02743

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/60 C07F5/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 118, no. 49, 11 December 1996, pages 12453-12454, XP000644320 LONG DAVID: "A catalytic system for rthylene polymerization..." see page 12454, column 1, line 48 - line 54 ---	1-7, 9-12,18
X	INORGANIC CHEMISTRY, vol. 32, no. 16, 4 August 1993, pages 3471-3477, XP000617663 RHEINGOLG: "(3-mesitylPz)3HB" see the whole document ---	10,11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 February 1997	21. 02. 97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Fischer, B

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	INORGANIC CHEMISTRY, vol. 34, no. 16, 4 January 1995, pages 4268-4270, XP000617666 HUANG: "(3,4-Ph2-5-Mepyrazolyl)3HB" see the whole document	1-18
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Y	EP,A,0 482 934 (THE DOW CHEMICAL) 29 April 1992 cited in the application see the whole document	1-18
X	EP,A,0 617 052 (ASAHI) 28 September 1994 cited in the application see claims 1,14 see page 17, line 52 - page 18, line 9 see page 30, line 57 - page 34, line 16 see page 42; examples 8,10	1-12,15, 18
X	INORGANIC CHEMISTRY, vol. 31, no. 19, 16 September 1992, pages 3871-4026, XP000617662 TROFIMENKO S.: "Spectroscopic analysis..." see experimental section page 3944 (LLL3, LLL7) see page 3944; figure 1	10,11
A	US,A,4 870 042 (KOHARA TADANAO) 26 September 1989 see page 3 - page 4; example 1 see claims 1-7	1
A	WO,A,94 01471 (EXXON) 20 January 1994 see page 20 - page 21; example 1	1

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INTERNATIONAL SEARCH REPORT

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Internat Application No
PCT/GB 96/02743

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